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Levels of PCDD/Fs, Dl-PCBs and HCB in Air, Soils and Sediments from a City with Multiple Thermal-Related Industries in China

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Abstract The levels of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), dioxin-like polychlorinated biphenyls (dl-PCBs) and hexachlorobenzene (HCB) were measured in various environmental compartments in Tangshan, China, which contains multiple thermal-related industries. The total toxic equivalent concentrations of these pollutants were 138 ± 87.2 fg/m^3 in air, 3.43 ± 2.88 pg/g in soils, and 1.42 ± 1.5 pg/g in sediments. The 2,3,7,8-PCDD/Fs profiles in atmospheric samples suggest that thermal-related industries are the most likely potential sources. Of the dl-PCBs, CB-77, CB-105 and CB-118 were the most abundant congeners and CB-126 was the dominant contributor to the TEQs from the dl-PCBs.

Keywords Thermal-related industries · POPs · Air · Soil · Sediment

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), dioxin-like polychlorinated biphenyls (dl-PCBs) and hexachlorobenzene (HCB) are the main unintentional persistent organic pollutants (POPs) identified in the Stockholm Convention. Previous studies have confirmed that these pollutants can be formed unintentionally during incineration or heat processing in some thermal-related industries, such as metallurgy, coking, power generation and cement production (Aries et al. 2006; Lin et al. 2007). Once released into the environment, these pollutants are stable and highly persistent, undergo long-range atmospheric transport and can be distributed in various environmental components including air, soil and sediments (Lohmann and Jones 1998).

Tangshan, in northern China, is the location of some of the most concentrated industrial activity in the country, and contains clusters of industrial plants. In particular, rich mineral deposits have helped to turn Tangshan into the biggest steel producer in China. The steel output in 2010 was about 68.3 million tons, which was about 4.9 % of the world's production. There are also more than 20 coking plants, five cement mills and several thermal power plants in the city. These industries have been identified as high potential sources of unintentional POPs such as PCDD/Fs, dl-PCBs and HCB (Liu et al. 2009; UNEP 2005). Extensive investigations have evaluated the POP concentrations in industrial areas. However, few studies on the contamination level of these pollutants have been carried out in a region involved in such a wide range of thermal-related industrial activities. In this study, the PCDD/Fs, dl-PCBs and HCB levels were investigated in air, soils and river sediments in Tangshan, with multiple thermal-related industries. The objective of this study was to evaluate the effects of emissions from these thermal-related industries on the environmental levels of these pollutants.

Materials and Methods

Tangshan is located in the east of Hebei Province, China, a total area of 13,472 km^2, and a population of 7.1 million. In this study, air, soil and sediment samples were collected from the industrial area of this city in June to August 2010. A map of the sampling locations is shown in Fig. 1. Air samples were collected using high volume samplers. The particulate phase PCDD/Fs, dl-PCBs and HCB were

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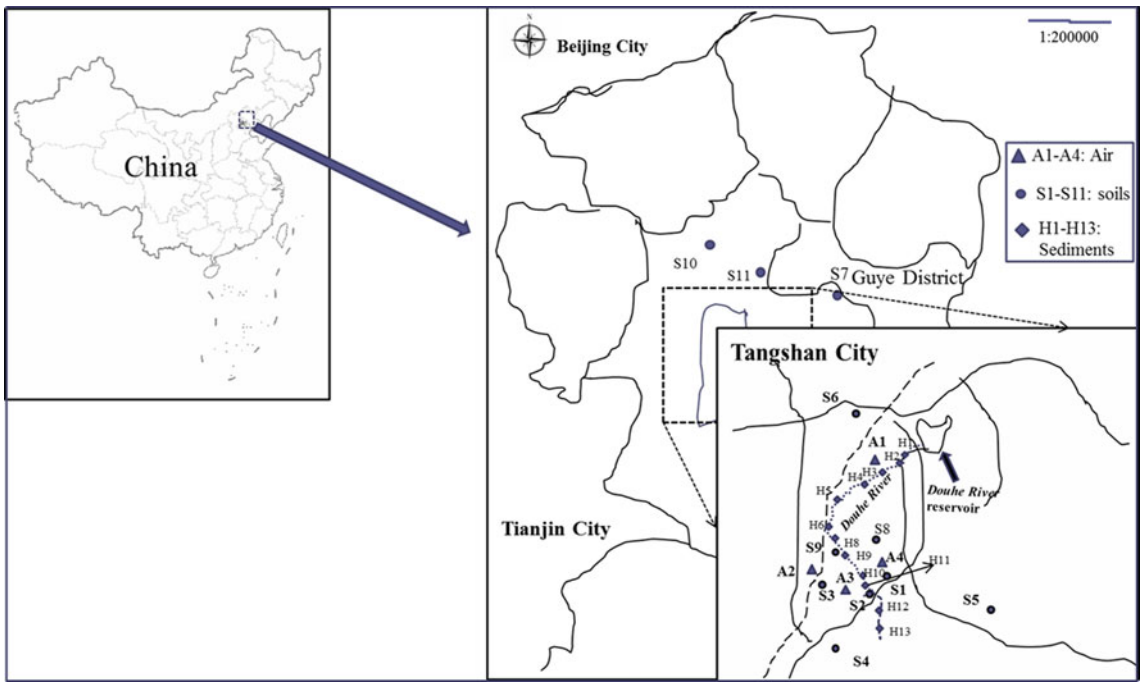

Fig. 1 Location of the sampling sites in Tangshan

collected on cleaned glass fiber filters (GFFs), and polyurethane foam (PUF) was used to absorb these pollutants in the gas phase. Four of the air-sampling sites were located in the industrial city based on the population distribution and the industrial layout, in locations where the multiple thermal-related sources could potentially have an impact. The control site was in a residential area 170 km from the industrial city and had no obvious pollution sources (not shown in Fig. 1). Surface soil samples (0–10 cm in depth) were collected at 11 sites in the industrial region and two sites in the control area. River Sediment samples were collected from 13 sites along the Douhe River, which is the main river running through Tangshan.

The US EPA methods 1613B and 1668A were used to measure the 2,3,7,8-PCDD/Fs and dl-PCBs. Briefly, prior to extraction, the GFFs and PUF plugs were combined for each sample, and 10 g of the dried soil and sediment samples were homogenized. All the samples were spiked with known amounts of $^{13}C_{12}$-labeled internal standards. The samples were then extracted with organic solvents by accelerated solvent extraction (ASE). The extracts were cleaned up on acid silica gel columns followed by multilayer silica columns. The PCDD/Fs and dl-PCBs were fractionated using basic alumina columns. Prior to analysis, the final extracts were spiked with $^{13}C_{12}$-labeled injection standards for recovery quantification. Analysis of the PCDD/Fs and dl-PCBs was carried out using a high resolution gas chromatograph and high resolution mass spectrometer (HRGC/HRMS). To analyze the samples for HCB, samples were spiked with a known amount of $^{13}C_6$-HCB and extracted by ASE. The extract was concentrated and further cleaned up on a 1:2 alumina/silica gel column. Prior to analysis by HRGC/HRMS, $^{13}C_{12}$ CB-15 was added to calculate the recovery.

For quality control, field and laboratory blanks were performed routinely and all results were within the limits specified for the various methods. The LOD for all analyses was defined as three times the signal/noise ratio. For concentrations below the LOD, a value of half the LOD was assigned for the calculation of total concentrations. The LOD values determined for this study were in the ranges of 3.2–13.9 fg/m^3 for air samples and 0.02–0.6 pg/g for soil/sediment samples. The recoveries of the ^{13}C-labelled internal standards ranged from 32 % to 124 %. The toxic equivalent concentrations (TEQs) for the PCDD/Fs and dl-PCBs were obtained using 2005 World Health Organization toxic equivalent factors (TEFs); while the TEQ for HCB was calculated according to the TEF reported by van Birgelen (1998).

Results and Discussion

Figure 2 summarizes the concentrations of the PCDD/Fs, dl-PCBs and HCB in atmospheric samples from the industrial city and the residential area. As shown in Fig. 2, HCB was the dominant POP on a mass basis, but the PCDD/Fs account for most of the TEQ. The average PCDD/F TEQ in samples from the industrial city was 116 ± 74 fg WHO-TEQ/m^3, while the TEQ in the residential area was 65 fg WHO-TEQ/m^3. The

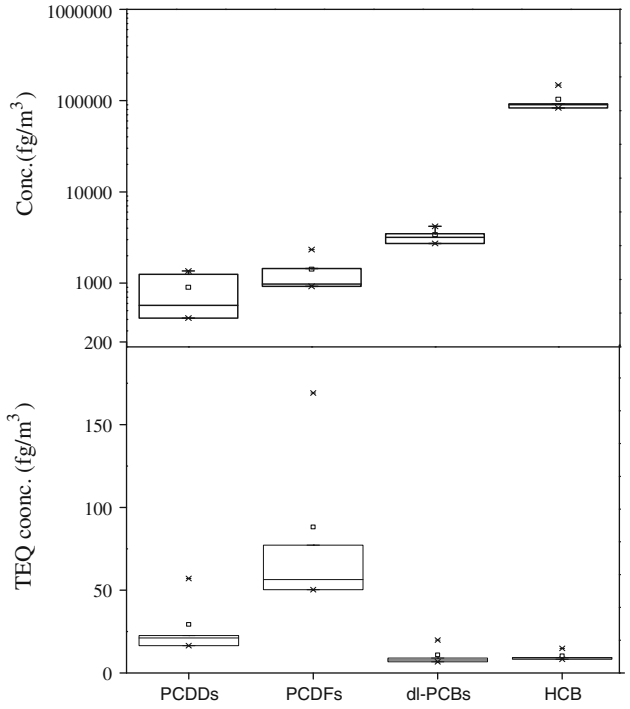

Fig. 2 Concentrations and TEQs of PCDD/Fs, dl-PCBs and HCB in ambient air samples from the industrial city

PCDD/F concentrations in air from the industrial city are generally consistent with the range for global urban/industrial areas (100–400 fg TEQ/m^3) reported by Lohmann and Jones (1998). Slightly higher concentrations were observed at sites in the industrial city than in the residential (control) area, but the difference was not statistically significant. The PCDD/F TEQs measured in this industrial city were comparable to those in an industrial area in Taiwan (150 fg I-TEQ/m^3) reported by Wang et al. (2007) and around a steel plant in Northeast China (3–247 fg I-TEQ/m^3; Li et al. 2010). A similar trend in the dl-PCB concentrations in air samples was also observed. The dl-PCB concentrations collected from the industrial city and the residential area were 11 ± 6 fg WHO-TEQ/m^3 and 6 fg WHO-TEQ/m^3, respectively. A good correlation was observed between the 2,3,7,8-PCDD/F and dl-PCB concentrations on a mass basis ($R = 0.87$).

The HCB concentrations in air samples from Tangshan was 104 ± 30 pg/m^3 on a mass basis. No difference was observed between the industrial city and the residential site (107 pg/m^3). In comparison with other areas of China, the HCB concentrations measured in this study are comparable to that in Qingdao (126 pg/m^3) and are also similar to the mean HCB concentration in China as a whole (near 100 pg/m^3; Wang et al. 2010).

These results indicate that although there are numerous potential POP sources from various thermal-related industries in Tangshan, the concentrations of these unintentional POPs in the air appear to be less serious than expected before the investigation. This may be due to the composition and properties of the raw materials used, the different combustion conditions under which the plants operate, or on-site pollution-control measures. Thus, this investigation might indicate that the release of unintentional POPs in the regions caused by similar thermal-related potential sources may vary from case to case.

Soils and sediments are known to be the main sink for airborne POPs. Due to their high persistence and slow biodegradation processes, POPs can accumulate in media containing organic matter such as soils and sediments. Thus, the concentrations of POPs in soil and sediment can provide information about long-term local contamination from these pollutants. In this study, the total TEQs of PCDD/Fs, dl-PCBs and HCB in Tangshan were 3.43 ± 2.88 pg/g in soils and 1.42 ± 1.5 pg/g in sediments respectively.

The average concentration of PCDD/Fs from 11 soil samples from the industrial city was 3 ± 2.6 pg WHO-TEQ/g, while the concentration in the residential area was 2.4 ± 0.45 pg WHO-TEQ/g. The PCDD/F concentrations from the soil samples in Tangshan are also comparable to those in other industrial areas worldwide (0.4–4.27 pg I-TEQ/g in Kocaeli, Turkey Bakoglu et al. 2005; and 0.1–1.08 pg I-TEQ/g in Spain Eljarrat et al. 2001). The Swedish soil guideline for PCDD/Fs is 10 pg TEQ/g, and based on this value, the soils from Tangshan do not appear to pose a health risk. In the sediment samples, lower PCDD/F concentrations were observed (1.1 ± 1.1 pg WHO-TEQ/g) than in the soil samples. However, among the sampling sites, somewhat higher concentrations were found in the lower reaches of Douhe River, where various industrial activities such as power generation and iron and steel smelting are located. This spatial distribution indicates that the industrial activities may contribute to the PCDD/F levels. Only limited studies are available on dl-PCB concentrations in soils and sediments in China. In this study, low concentrations of dl-PCBs were present, with values of 0.13 ± 0.05 pg WHO-TEQ/g and 0.07 ± 0.05 pg WHO-TEQ/g in the soils and sediments, respectively.

The average HCB concentration in soils from the industrial city was 3 ± 2.27 ng/g, which is lower than in the residential area (4 ± 2.15 ng/g). This result indicates that HCB is ubiquitous in environmental matrixes and does not appear to be directly influenced by the industries in Tangshan. There have been some studies on the HCB in sediments in China (Wang et al. 2010), including the Yangtze River (0.94–1.82 ng/g), the Huangpu River (3.2 ng/g) and Taihu Lake (0.06–9.69 ng/g). In this study, the average concentration of 13 samples from the Douhe River was 2.5 ± 3.5 ng/g, which is consistent with levels in other parts of China.

The 2,3,7,8-PCDD/F and dl-PCB homologue profiles in samples from the industrial city are shown in Fig. 3. For PCDD/Fs, the homologue profile indicates that highly

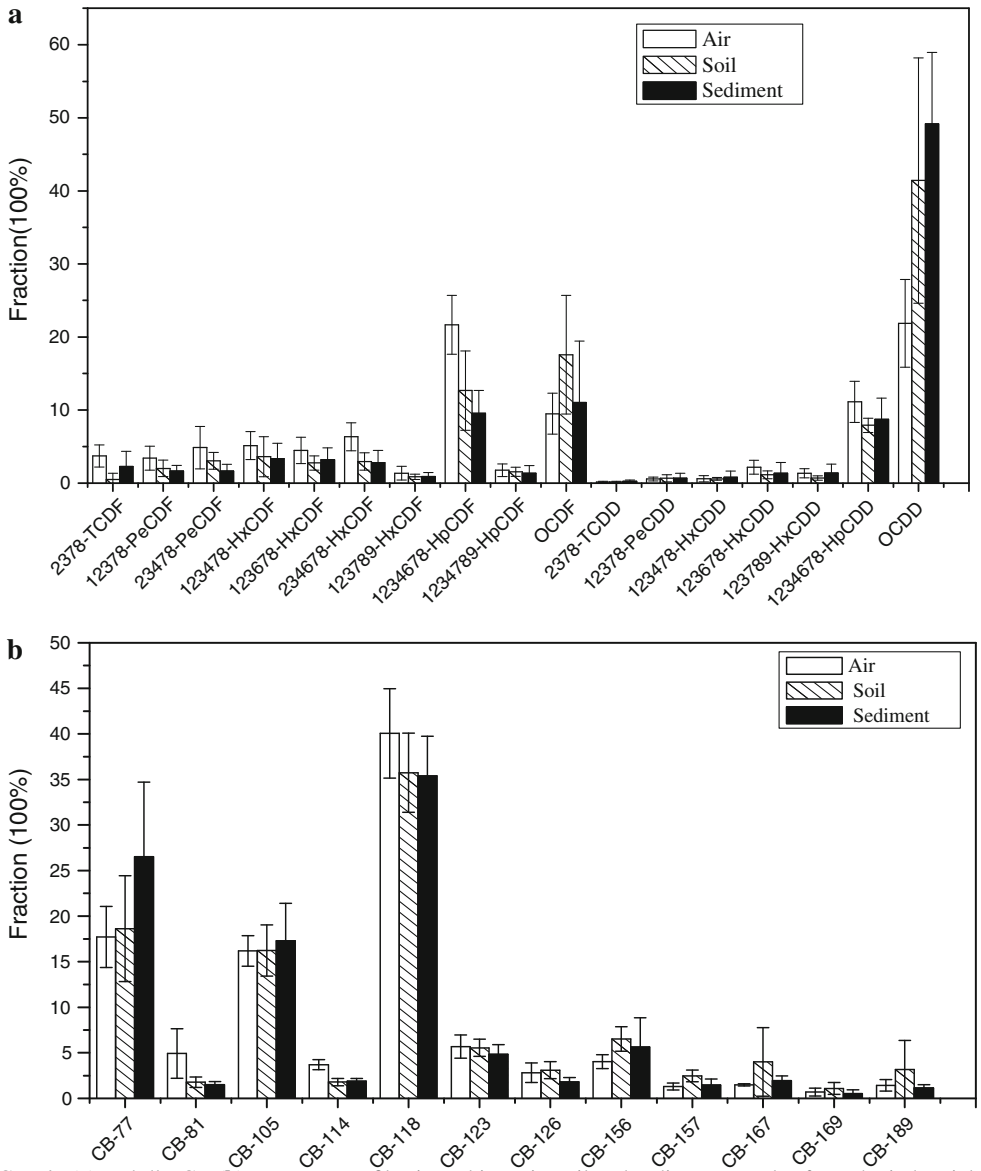

Fig. 3 Average PCDD/F (**a**) and dl-PCB (**b**) congener profiles in ambient air, soil and sediment samples from the industrial city (*bars* indicate data standard deviation)

chlorinated congeners were dominant, with 1,2,3,4,6,7,8-HpCDD, OCDD, 1,2,3,4,6,7,8-HpCDF, and OCDF comprising 65 %–79 % of the total 2,3,7,8-PCDD/Fs. In the air samples, the PCDF concentrations were higher than the PCDD concentrations. This congener pattern is similar to those reported for some thermal-related industries such as sintering and coking processes (Liu et al. 2009; Xhrouet et al. 2001), indicating the potential influence of the thermal-related industries on the atmospheric PCDD/F concentrations. PCDD/F congener patterns in the soils and sediments were clearly different from those in the air. PCDF/PCDD ratio decreased, and a reduction in the percentages of PCDFs was observed with decreasing levels of chlorination. However, the contribution of OCDD to the PCDD/Fs was considerably larger than for air. In contrast to the congener pattern in air, which was the directly affected by the thermal-related industries, the homologue patterns in soils and sediments can be explained by the different atmospheric precipitation and transportation abilities of the congeners. The highly chlorinated congeners, especially OCDD which was the predominant congener in this study, have very low vapor pressures and are highly hydrophobic, so they have a greater tendency to bind to organic matter in soil and sediment.

Of the dl-PCBs, CB-118 was the dominant congener, followed by CB-105 and CB-77, and these three congeners together contributed more than 70 % of the total dl-PCBs (Fig. 3b). Due to its much higher TEF value than other

dl-PCB congeners, CB-126 was the main toxic contributor, contributing more than 85 % of the total dl-PCB toxicity.

Overall, the levels of PCDD/Fs, dl-PCBs and HCB measured in air, soils and sediments from Tangshan are similar to or lower than concentrations in other areas of the world, This result implies that the multiple thermal-related industries might not have a major effect on the surrounding environment and the total contribution of these sources to the unintentional POP concentrations is negligible in Tangshan. As a case study, the data obtained during this work would be useful to understand unintentional POPs emissions from thermal-related industries and their impact on the regional environments to allow for appropriate pollution control measures in the future.

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